



# Site-selective Pt dewetting on WO<sub>3</sub>-coated TiO<sub>2</sub> nanotube arrays: An electron transfer cascade-based H<sub>2</sub> evolution photocatalyst

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## ABSTRACT

Among several parameters that affect the yield of a photocatalytic process mediated by a metal oxide semiconductor, key is the efficient separation and transfer of photo-generated charge carriers. To overcome kinetic limitations and enable charge transfer, an effective strategy is to decorate the photocatalyst surface with cocatalytic nanoparticles of either a second semiconductor metal oxide or a noble metal. Nevertheless, classical deposition techniques based on powder technology approaches lead to randomly placed cocatalytic nanoparticles at the photocatalytic surface. The poor control over cocatalyst placement can drastically hamper the photocatalytic efficiencies, and can also prevent a full understanding of the charge carrier dynamics and photocatalytic mechanism. Here we investigate a highly defined charge separation platform for photocatalytic H<sub>2</sub> evolution based on a Pt-WO<sub>3</sub>-TiO<sub>2</sub> “stacked” structure constructed on anodically grown TiO<sub>2</sub> nanotube arrays. Key is the formation of a site-selective and sequential W and Pt metal sputter-decoration only at the mouth of highly-ordered TiO<sub>2</sub> nanotubes. After placing the W-Pt bilayer at the nanotubes mouth, a suitable thermal treatment forms a WO<sub>3</sub> layer atop the nanotubes while the Pt film undergoes solid state dewetting into 2–6 nm-sized Pt nanoparticles. These structures show strongly improved photocatalytic H<sub>2</sub> evolution efficiency compared to any other single-cocatalyst system (Pt-TiO<sub>2</sub> and WO<sub>3</sub>-TiO<sub>2</sub>) and pristine TiO<sub>2</sub> nanotubes. The photocatalytic activity improvement is ascribed to an enhanced charge carrier separation mechanism enabled by the well-defined TiO<sub>2</sub>-WO<sub>3</sub>-Pt architecture that provides swift electron transfer through WO<sub>3</sub> and towards Pt for H<sub>2</sub> evolution.

## 1. Introduction

Since the pioneering work of Fujishima and Honda [1] in 1972, the production of H<sub>2</sub> by photocatalytic splitting of H<sub>2</sub>O on semiconductors has been extensively investigated. Among the different studied photocatalysts, titanium dioxide (TiO<sub>2</sub>) received large attention owing to its suitable conduction (CB) and valence band (VB) edge positions, as well as for its nontoxicity and stability against corrosion and photo-corrosion [2,3]. The bottom of TiO<sub>2</sub> conduction band (CB) lies higher than the redox potential of water (−0.45 and 0 V vs. NHE, respectively, at pH 0) [4]. Therefore, by promoting electrons in TiO<sub>2</sub> CB through UV light irradiation ( $E_{\text{g TiO}_2} \sim 3.0\text{--}3.2\text{ eV}$ ), it is possible to reduce H<sub>2</sub>O to H<sub>2</sub>.

However, pristine TiO<sub>2</sub> shows low efficiencies for H<sub>2</sub> production because of trapping and recombination of charge carriers, and owing to a kinetically slow electron transfer to reactants. Nanostructured photocatalysts can be employed in order to improve the electron transfer efficiency. Particularly, one-dimensional (1D) nanostructures, such as

anodic TiO<sub>2</sub> nanotubes (NTs), have attracted great attention in the last decades [5–7]. Vertically aligned arrays of self-organized NTs can be grown by a simple anodization of Ti metal in a suitable electrolyte [2,3,8]. The electrochemical conditions can be adjusted in order to lead to a large palette of nanotubular morphologies [8,9]. These highly-ordered 1D TiO<sub>2</sub> structures can promote directional charge transport and orthogonal electron-hole separation that allow for enhanced photoelectrochemical and photocatalytic performances [3,10].

In addition, cocatalysts that aid charge separation and transfer by forming a heterojunction on TiO<sub>2</sub>, such as a suitable semiconductor or noble metal nanoparticles (e.g. Au, Pd, Pt) can be also employed to further improve the performance of titania-based photocatalysts.

In view of constructing a composite photocatalyst, a particularly interesting constellation is obtained when TiO<sub>2</sub> is combined to WO<sub>3</sub>, an n-type semiconductor with a band gap  $E_{\text{g WO}_3} \sim 2.6\text{--}2.8\text{ eV}$  [11,12]. With such a combination, a favorable band alignment at the TiO<sub>2</sub>-WO<sub>3</sub> interface is generated that enables efficient charge separation [13] by

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transfer of  $\text{TiO}_2$  CB electrons into the  $\text{WO}_3$  CB [14–17]. The photocatalytic enhancement obtained when  $\text{WO}_3$  is combined to  $\text{TiO}_2$  is frequently discussed in terms of  $\text{WO}_3$  contribution to visible-light absorbance ( $\lambda_{\text{abs WO}_3} < \sim 450 \text{ nm}$  – i.e. larger photon harvesting) [18,19], enhanced surface acidity that can yield improved adsorption of reactants [20–25], higher hydrophilicity [26], and the possibility of enabling a “z-scheme” for charge separation [27].

While the placement of a suitable metal oxide semiconductor ( $\text{WO}_3$ ) at the  $\text{TiO}_2$  surface can enhance charge-separation, localized Schottky-type junctions are also commonly formed by placing noble metal cocatalytic nanoparticles on the individual oxides. For example, Pt is typically a most efficient cocatalyst for the  $\text{H}_2$  generation reaction [28–31]. Pt nanoparticles at the  $\text{TiO}_2$  surface can enable efficient electron transfer at the catalyst/environment interface by providing a favorable solid state junction to  $\text{TiO}_2$  [4], hence improving the electron transfer to reactants while additionally catalyzing hydrogen atom recombination reaction, and thus facilitating  $\text{H}_2$  gas formation ( $2\text{H}^\circ \rightarrow \text{H}_2$ ) [32,33].

These two cocatalyst principles, i.e. a charge separation cocatalyst ( $\text{WO}_3$ ) and a charge transfer cocatalyst (Pt), can, based on an anticipated synergistic effect, be combined into a composite photocatalyst, e.g. in a  $\text{TiO}_2$ - $\text{WO}_3$ -noble metal combination. The benefit of combining these three catalytic elements has been used also in thermal catalysis, e.g. by using  $\text{TiO}_2$ - $\text{WO}_3$ -Pt composites as de- $\text{NO}_x$  catalysts [34].

In some recent studies, such as the work of Pap et al.,  $\text{TiO}_2$ - $\text{WO}_3$ -noble metal (Au, Pt) powders were investigated in view of their photocatalytic performance [35–38]. These works pointed out the potential of combining the two cocatalyst principles for efficient photocatalysis, but the chosen preparation method, based on a classical powder technology process, suffers from a poor control over morphology and stacking of the cocatalysts. Particularly, only a loose and undefined contact (junction) between the two oxides can be obtained – this hampers the charge carrier separation: note that in these works any noble metal- $\text{WO}_3$ - $\text{TiO}_2$  combination was found to be less photocatalytically active for  $\text{H}_2$  evolution than a simple noble metal- $\text{TiO}_2$  configuration.

Moreover, similar synthesis methods for noble metal- $\text{WO}_3$ - $\text{TiO}_2$  structures lead in general to a photocatalyst configuration characterized by undefined interfaces, which can bring about an uncontrolled charge carried dynamics and various different photocatalytic mechanisms – in other words, given that a photocatalytic enhancement can be observed, an accurate understanding of the photocatalytic mechanism is almost impossible.

In contrast, with the present work, we introduce a defined and reliable fabrication strategy of a synergistic Pt- $\text{WO}_3$ - $\text{TiO}_2$  photocatalyst for  $\text{H}_2$  generation constructed with nanoscale precision on an array of highly-ordered  $\text{TiO}_2$  nanotubes. This architecture, owing to its highly-defined geometry obtained by site-selective placement of Pt and  $\text{WO}_3$  cocatalysts, induces an electron transfer cascade from the  $\text{TiO}_2$  NTs (light absorber) to the  $\text{WO}_3$  junction (charge separation cocatalyst) and onward to the Pt nanoparticles (NPs) (charge transfer cocatalyst). The result is a facilitated electron transport towards the nanotube top for  $\text{H}_2$  evolution, while the uncoated bottom of the  $\text{TiO}_2$  cavities is a suitable site for hole-mediated oxidation reaction. We show that, in contrast to previous works, a morphologically controlled  $\text{TiO}_2$ - $\text{WO}_3$ -Pt design leads to enhanced photocatalytic  $\text{H}_2$  evolution efficiencies, which are higher than those measured for classic noble metal- $\text{TiO}_2$  photocatalysts.

## 2. Experimental

### 2.1. Fabrication of the $\text{TiO}_2$ nanotube array

Ti foils (Advent Research Materials, 0.125 mm thickness, 99.6 + % purity) were degreased by sonicating in acetone, ethanol, and deionized water, and were then dried in a  $\text{N}_2$  stream. Then, the Ti foils were anodized to fabricate the highly ordered  $\text{TiO}_2$  nanotube arrays in a hot

electrolyte based on 3 M HF in o- $\text{H}_3\text{PO}_4$  (Sigma- Aldrich) [39]. For the anodic growth, a two-electrode configuration was used, where the Ti foil (15 mm  $\times$  15 mm) and a Pt sheet were the working and counter electrodes, respectively. The anodization experiments were carried out by applying a potential of 15 V (for 2 h) using a DC power supply (VLP 2403 Voltcraft). After anodization, the  $\text{TiO}_2$  nanotube arrays on Ti metal substrates were rinsed with ethanol and dried under  $\text{N}_2$  stream.

### 2.2. W and Pt sputtering-coating and thermal treatment

In order to site-selectively place the cocatalytic Pt/ $\text{WO}_3$  stack only atop the nanotubes, a plasma-sputtering machine (EM SCD 500, Leica) was used in a shallow angle configuration to sputter-coat W and Pt metal thin films (W-Pt bilayers) using a 99.8% pure W target (Hauner Metallische Werkstoffe) and a 99.99% pure Pt target (Hauner Metallische Werkstoffe), respectively. The applied sputtering current was 16 mA and the pressure of the sputtering chamber was set at  $10^{-2}$  mbar of Ar. The amount of sputtered material was in-situ determined by an automated quartz crystal monitor, and is reported in this work as nominal thickness of the sputtered film. In previous work the deposition process for Pt was calibrated, and a linear correlation was found between the nominal thickness of the sputtered layer (in nm) and the actual loading on the catalyst (in  $\mu\text{g}_{\text{Pt}}$ ) [28,40]. The Pt loading determined by ICP-OES measurements scales with the nominal thickness of the sputtered layer with a factor of  $1.1 \mu\text{g}_{\text{Pt}} \text{ nm}^{-1}$ . In this work, the sputter-coated Pt films have a nominal thickness of 1 nm, and are coated on an active surface (irradiated photocatalyst surface) of  $0.78 \text{ cm}^2$ . Thus, for Pt-led structures, the Pt loading is  $\sim 1.4 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ .

The Pt film nominal thickness of 1 nm was selected based on previous works demonstrating that a thickness of the sputter-coated noble metal film  $< 5 \text{ nm}$  leads after dewetting to optimized cocatalyst loading and photocatalytic efficiency. In some cases, it was found that minimal amounts as low as e.g. 1 nm can lead to a highest  $\text{H}_2$  evolution rate [28].

Subsequently, the samples were annealed at  $450^\circ\text{C}$  in air for 1 h, using a Rapid Thermal Annealer (Jipelec Jetfirst 100 RTA), with a heating and cooling rate of  $30^\circ\text{C min}^{-1}$ . The thermal treatment formed a  $\text{WO}_3$  layer on the  $\text{TiO}_2$  nanotube arrays onto which the Pt film splits into nanoparticles by thermal dewetting.

### 2.3. Characterization of the structures

A field-emission scanning electron microscope (FE-SEM, Hitachi S4800) and a high resolution transmission electron microscope (HR-TEM, Philips CM300) were used to characterize the morphology of the samples. Sample chemical composition analysis as well as valence band measurements were carried by X-ray photoelectron spectroscopy (XPS, PHI 5600, US). XPS spectra were acquired using Al X-ray source. The XPS spectra were corrected in relation to the  $\text{Ti}2p$  signal at  $458.5 \text{ eV}$ . PHI MultiPak<sup>™</sup> software and database were used for quantitative analysis. X-ray diffraction (XRD) with an X'pert Philips MPD (equipped with a Panalytical X'celerator detector) was employed to examine the crystallographic properties of the materials. The light absorption properties (diffuse reflectance, DR) of the samples were measured by a UV-vis Spectrophotometer (Lambda 950, PerkinElmer).

### 2.4. Photocatalytic experiments

The photocatalytic  $\text{H}_2$  generation measurements were carried out by irradiating the oxide films with UV light (LED Opsytec,  $\lambda = 365 \text{ nm}$ , beam size =  $0.78 \text{ cm}^2$ , power of  $80 \text{ mW cm}^{-2}$ ) in a 20 vol% ethanol–water solution (ethanol was used as hole-scavenger) in a quartz tube sealed with a gas-tight cap. The ethanol-water solution (kept under static conditions during the runs) and the cell head-space (volume =  $6.22 \text{ mL}$ ) were purged with  $\text{N}_2$  gas for 15 min prior to photocatalysis.  $\text{N}_2$ -purging is needed as  $\text{O}_2$ , if present, would reduce the

efficiency of  $\text{H}_2$  generation by competitively reacting with conduction band electrons forming  $\text{O}_2^{\cdot -}$ .

The amount of produced  $\text{H}_2$  (which was accumulated over the irradiation time in the head space of the tube) was measured by using a gas chromatograph (GCMSQ02010SE, Shimadzu) equipped with a thermal conductivity detector and a Restek micropacked Shin Carbon ST column ( $2\text{ m} \times 0.53\text{ mm}$ ). GC measurements were carried out at a temperature of the oven of  $45^\circ\text{C}$  (isothermal conditions), with the temperature of the injector set at  $280^\circ\text{C}$  and that of the TCD fixed at  $260^\circ\text{C}$ . The flow rate of the carrier gas, i.e., argon, was  $14.3\text{ mL min}^{-1}$ . The majority of the experiments lasted 5 h, and the amount of evolved  $\text{H}_2$  was measured at the end of the experiments. Photocatalytic measurements of Acid Orange 7 (AO7) degradation were carried out with the same instrumental setup and using a  $0.125\text{ mM}$  AO7 solution. The light absorbance of the solution was measured by using a UV–vis spectrophotometer (Lambda XLS+, Perkin Elmer) at  $485\text{ nm}$  wavelength (maximum absorbance value) in order to determine the AO7 concentration.

### 3. Results and discussion

Fig. 1a shows the morphology of the highly-ordered anodic  $\text{TiO}_2$  NTs used in this work, which are grown on Ti metal foils by anodization in a hot  $\text{H}_3\text{PO}_4/\text{HF}$  electrolyte [39]. These NTs have an almost ideal hexagonal packing, an average inner diameter of  $\sim 80\text{--}90\text{ nm}$  and a length of  $\sim 190\text{--}200\text{ nm}$  (see Inset in Fig. 1a). This well-defined structure with short aspect-ratio allows for the site-selective decoration of only the NT top, with e.g. metal bilayers (Pt and W in this work) using a grazing-angle sputtering technique.

After the sputter-deposition of a metal film, e.g. a  $1\text{ nm}$ -thick Pt film, a thermal treatment is carried out to crystallize the  $\text{TiO}_2$  NTs. Worth nothing, as illustrated in Fig. 1b, such a thermal treatment leads at the same time to solid state dewetting of Pt, that is, to the conversion of the sputtered Pt film into Pt nanoparticles, with spherical shape and average diameter of  $2\text{--}6\text{ nm}$  (as shown in Fig. 1c and d). The driving

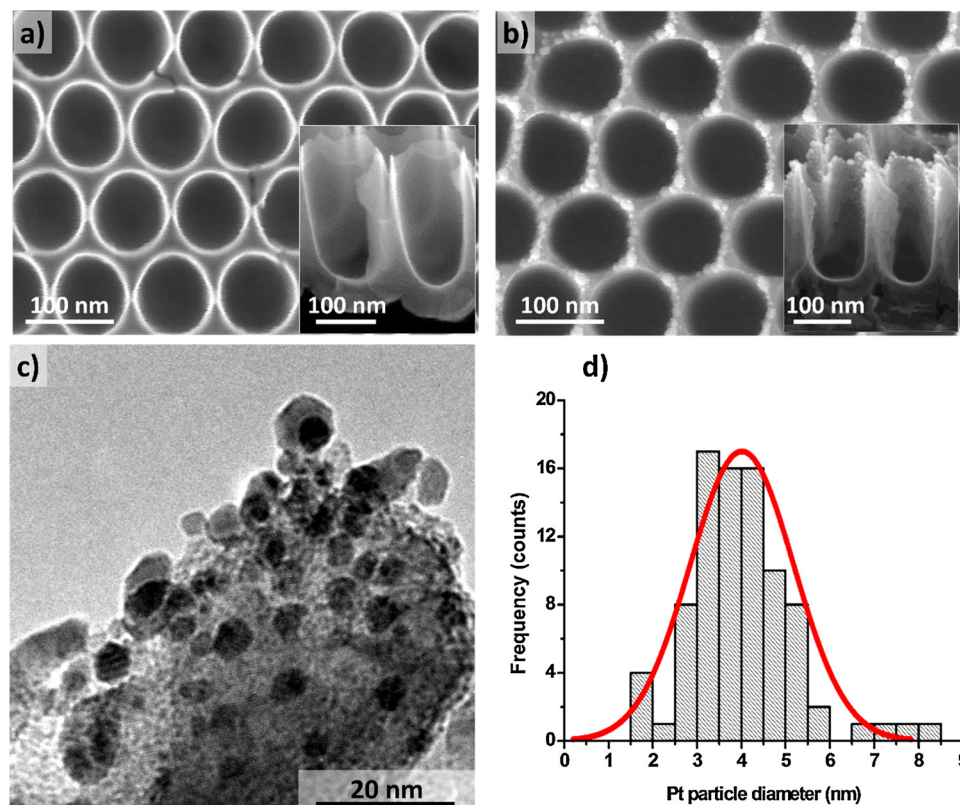
force for dewetting [41] is the minimization of the free surface energy of the metal (Pt) film, of the substrate (oxide surface) and of the metal-substrate interface (Pt/oxide). Since the thinner the metal film the higher its surface-to-volume ratio and thus its surface energy, the dewetting of e.g. few nm-thick metal films can occur also at temperature far below the metal melting point – that is, the film can dewet while remaining in the solid state [42].

The NT structures can also be decorated by sputtering a W film firstly (nominal thickness of  $0\text{--}30\text{ nm}$ ), followed by sputter-deposition of a thin Pt metal layer (nominal thickness of  $1\text{ nm}$ ) – i.e. using a sequential metal sputter-coating approach that form a W-Pt bilayer at the  $\text{TiO}_2$  NT surface. A subsequent thermal treatment of these structures in air at  $450^\circ\text{C}$  for 1 h forms the architectures illustrated in Fig. 2 (additional SEM images for these structures are reported in Fig. S1).

In the case of small amounts of shallow-angle sputtered W (nominal thickness  $< 10\text{ nm}$ , e.g. Fig. 2a and b), it is possible to observe from the cross-sectional SEM picture (Fig. 2b) that the deposition of the W film occurs only at the rim of the tubes, thus leaving the tube bottom uncovered (providing free  $\text{TiO}_2$  surface). However, for thicker W films ( $\geq 10\text{ nm}$ , Fig. 2c and d) a certain amount of W is deposited also deep in the NTs – e.g. Fig. 2d shows that  $\text{WO}_3$  is formed also close to the NT bottom.

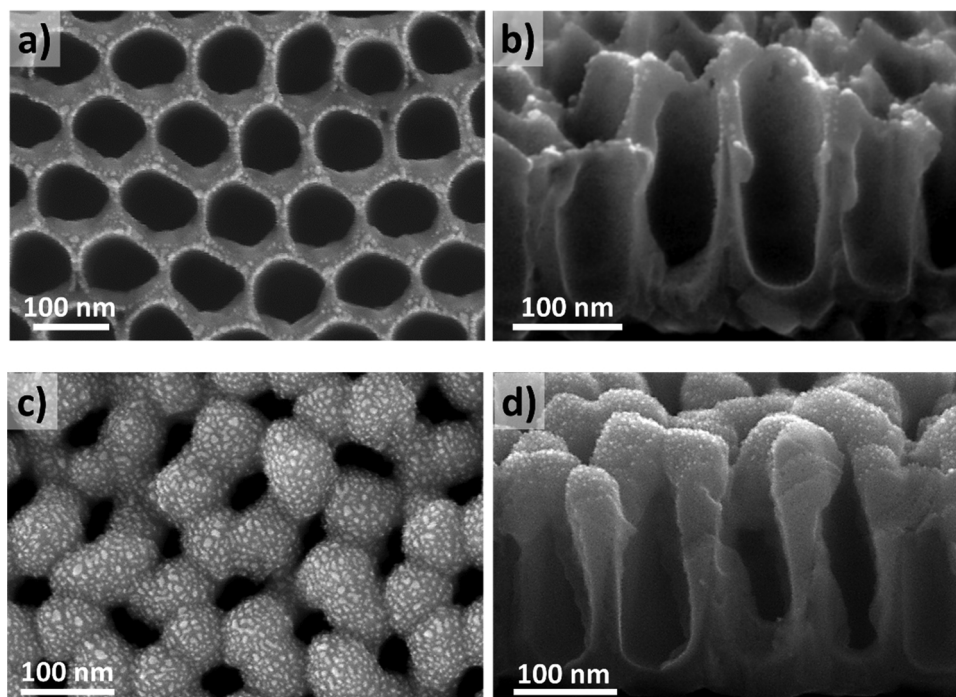
The structures in Figs. 1 and 2 were characterized by XRD, HR-TEM in view of their composition and structure. The results are compiled in Fig. 3a,b. The intense XRD peaks (Fig. 3a) at  $2\theta = 25.4^\circ$  and  $27.6^\circ$  can be assigned to  $\text{TiO}_2$  (101) anatase and (110) rutile reflections [43,44], respectively, while peaks at  $2\theta \sim 23\text{--}24^\circ$  can be ascribed to the monoclinic  $\text{WO}_3$  phase [45]. The relatively intense reflections at  $2\theta \sim 23\text{--}24^\circ$  observed for the structure 1Pt-30 $\text{WO}_3$ - $\text{TiO}_2$  is well in line with the larger amount of sputtered W metal (additional XRD patterns are shown in Fig. S2). In any case, no XRD signal for Pt can be seen, owing to the small amount of sputtered noble metal.

The TEM images in Fig. 3b clearly show the decoration of the top of the tubes with the two cocatalyst (i.e. Pt and  $\text{WO}_3$ ). The HR-TEM images (insets in Fig. 3b) reveal the presence of both anatase  $\text{TiO}_2$  (101)

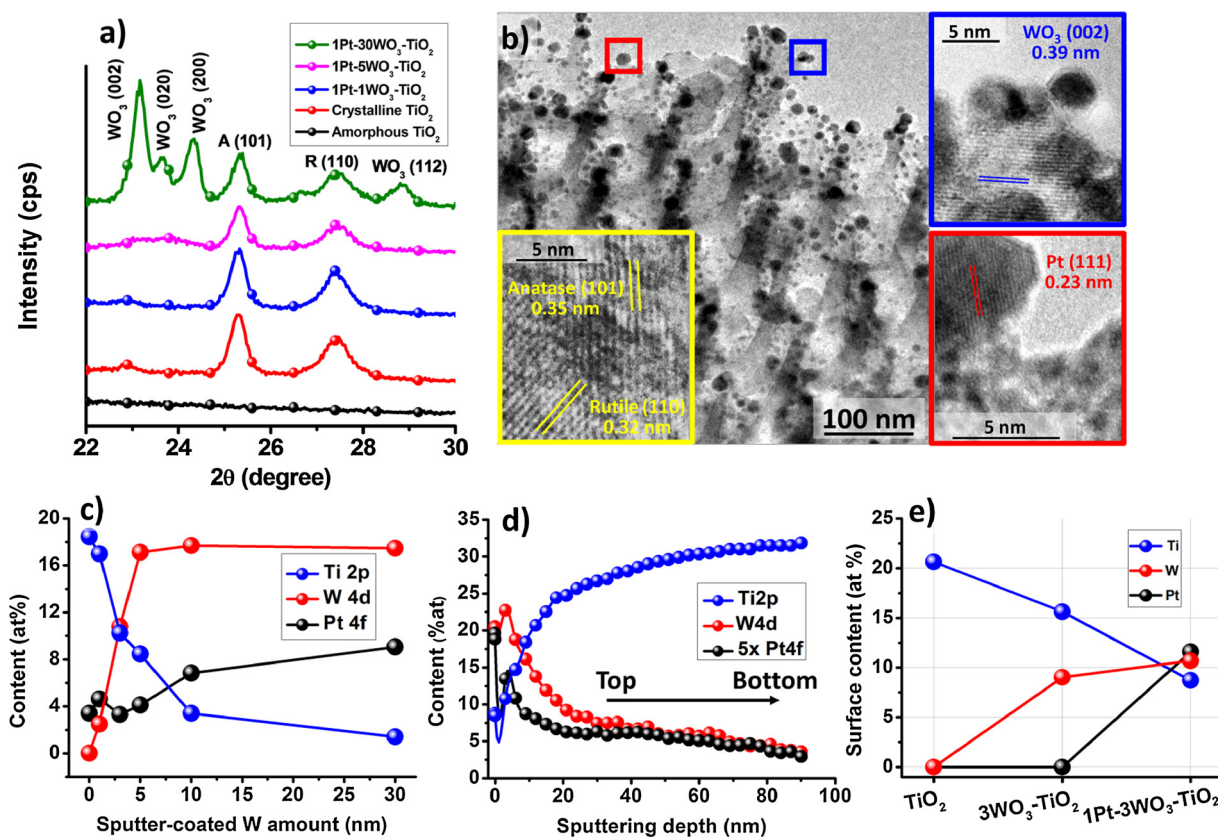


**Fig. 1.** (a–b) SEM images of various  $\text{TiO}_2$  structures: (a) arrays of pristine  $\text{TiO}_2$  nanotubes. Inset: cross-sectional view of the pristine NTs; (b)  $\text{TiO}_2$  NTs coated with a sputtered  $1\text{ nm}$ -thick Pt film after dewetting (thermal treatment at  $450^\circ\text{C}$ , air, 1 h). Inset: cross sectional view. (c) TEM image of the very top of a nanotube decorated with a sputtered-dewetted  $1\text{ nm}$ -thick Pt film; (d) Pt NP size distribution.





**Fig. 2.** (a, c) Top and (b, d) cross sectional SEM images of  $\text{TiO}_2$  NTs coated with (a, b) 5 nm-thick and (c, d) 30 nm-thick W film and then with Pt (1 nm-thick). All the structures were subjected to thermal treatment and dewetting.



**Fig. 3.** (a) Magnified view of the XRD patterns showing the main reflections of anatase (A) and rutile (R)  $\text{TiO}_2$  and monoclinic  $\text{WO}_3$ , (XRD patterns measured in the  $20$ – $80^\circ$   $2\theta$  range are in Fig. S2). (b) TEM images of sample 1Pt-5 $\text{WO}_3$ - $\text{TiO}_2$ . Insets: HR-TEM images: (yellow) crystal planes of (101) anatase  $\text{TiO}_2$  and (110) rutile  $\text{TiO}_2$  in the sidewalls and bottom of the nanotubes; (blue) crystal planes of (002) monoclinic  $\text{WO}_3$  and (red) crystal planes of (111) cubic Pt at the very top of the nanotubes. (c, d and e) Ti, W and Pt content determined from XPS analysis: (c) surface content as a function of the nominal thickness of the sputter-coated W films, (d) depth profile (content measured along the depth of the nanotubes; the Pt signal in the plot is magnified by a factor 5x) and (e) Ti, W and Pt surface content of three differently decorated  $\text{TiO}_2$  NT layers showing the change in surface composition after the different steps of the W and Pt sputter deposition approach and thermal treatment (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

and rutile  $\text{TiO}_2$  (110) in the sidewalls and bottoms of the tubes, and, confirm the site-selective placement of the monoclinic  $\text{WO}_3$  layer and Pt NPs on the top of the tubes. For example, the HR-TEM image in the blue box in Fig. 3b clearly shows the  $\text{WO}_3$  lattice planes – in the same image one can also identify, owing to a clearly different contrast, various Pt nanoparticles of a size distribution that is in line with that shown in Fig. 1d. Thus, SEM analysis along with XRD and TEM results (as well as XPS data below) confirm the presence of Pt nanoparticles as well as the conversion of the sputtered W metal to crystalline  $\text{WO}_3$  layer atop the architecture.

XPS analysis was carried out to investigate the composition of these structures and to gain information of the interfaces constructed in the Pt/ $\text{WO}_3$ / $\text{TiO}_2$  cocatalytic stack. The XPS surveys (Fig. S3a) show that the structures are composed of Ti, O, W and Pt, with small traces of adventitious carbon and P (due to the anodization in highly-concentrated  $\text{o-H}_3\text{PO}_4$ ). The XPS doublet with signals peaking at  $\sim 71.3$  and  $74.7$  eV (Fig. S3b) can be assigned to  $\text{Pt}4f_{7/2}$  and  $\text{Pt}4f_{5/2}$ , respectively [46], and confirms the metallic state of the dewetted Pt nanoparticles. The XPS doublet peaking at  $\sim 36.5$  and  $38.7$  eV (Fig. S3c) can be attributed to  $\text{WO}_3$  [47,48]. Note that in contrast to what is observed for Pt (i.e. solid-state thermal dewetting leading to rupture of the Pt film into Pt NPs), the sputter-coated W film is subjected to a different fate when annealed in air: it reacts with  $\text{O}_2$  gas (thermal oxidation) and forms a crystalline  $\text{WO}_3$  layer atop the NTs [49].

The XPS data reported in Fig. 3c show that the  $\text{Ti}2p$  signal for the NT structures decreases with increasing the amount of sputtered W. This is well in line with data in Fig. S3d, and indicates that the  $\text{WO}_3$  layers formed from W sputtered films  $> 10$  nm cover almost totally the  $\text{TiO}_2$  NT surface. The weak Ti signal is in this case attributed to the uncovered  $\text{TiO}_2$  surface at the very bottom of the tubes. A side effect of sputter-coating W film  $> 5$  nm is the increase of the surface content of Pt at the top of the structures. This can be ascribed to the narrowing of the tube mouth (as clearly shown in Fig. 2c and d). Hence, the relatively large amount of deposited W makes available a larger surface on the top of the cavities for Pt deposition.

The XPS depth profiling (Fig. 3d) corroborates the stacked architecture of the photocatalyst, with the presence of Pt and  $\text{WO}_3$  only at the very top of the tubes, i.e. the signals of Pt and W decrease sharply from the NT top towards the bottom of the cavities.

The XPS data in Fig. 3e show the change in surface composition after each step of sputter-deposition and thermal treatment, i.e. in order to form the structures  $3\text{WO}_3\text{-TiO}_2$  and  $1\text{Pt-WO}_3\text{-TiO}_2$ . The Ti signal drops significantly after the sequential W and Pt sputter coating, confirming that the  $\text{WO}_3$  layer firstly and then the Pt nanoparticles are deposited atop the  $\text{TiO}_2$  nanotubes. Moreover, the amount of W in  $1\text{Pt-WO}_3\text{-TiO}_2$  and  $\text{WO}_3\text{-TiO}_2$  is comparable, which confirms not only the reliability of the cocatalyst deposition method (fine control over amount and placement), but also that Pt cocatalyst is deposited atop the nanotube structure. The atomic concentration of the various elements in the structures are summarized in Table S1.

In order to evaluate the interaction of Pt,  $\text{WO}_3$  and  $\text{TiO}_2$  with each other at the different formed interfaces, the high resolution XPS spectra in the  $\text{W}4f$  and  $\text{Pt}4f$  regions for different structures ( $\text{TiO}_2$ ,  $\text{Pt-TiO}_2$ ,  $\text{WO}_3\text{-TiO}_2$  and  $\text{Pt-WO}_3\text{-TiO}_2$ ) are overlaid in Fig. S4a and b, respectively. The W state (Fig. S4a) is virtually identical in  $\text{WO}_3\text{-TiO}_2$  and  $\text{Pt-WO}_3\text{-TiO}_2$ . The peak at  $36.48$  eV observed for pristine  $\text{TiO}_2$  is ascribed to the  $\text{Ti}3p$  signal, which falls in the  $\text{W}4f$  signal region. Also, as it is evident from Fig. S4b, Pt is present in its metallic form, and no shift could be detected in the  $\text{Pt}4f$  doublets of  $\text{Pt-TiO}_2$  and  $\text{Pt-WO}_3\text{-TiO}_2$  structures. In other words, the XPS data confirm the stacked architecture of the  $\text{Pt-WO}_3$  cocatalyst atop the NTs, and the sequential deposition of the  $\text{WO}_3$  and Pt cocatalytic elements does not affect their chemical state, which is for each element comparable in the different structures.

These structures were assessed in view of their photocatalytic  $\text{H}_2$  evolution performance, from water-ethanol (20%) solution under UV light irradiation (LED light, 365 nm). The results are shown in Fig. 4a–c.

From these data it is clear that, for these stacked structures, an optimized amount of sputtered W leads to significantly higher photocatalytic  $\text{H}_2$  generation efficiency than any other combination ( $\text{Pt-TiO}_2$ ,  $\text{WO}_3\text{-TiO}_2$ ) or pristine  $\text{TiO}_2$ . More precisely, both pristine  $\text{TiO}_2$  NTs ( $\text{TiO}_2$ ) and  $\text{TiO}_2$  NTs modified only with  $\text{WO}_3$  ( $3\text{WO}_3\text{-TiO}_2$ ) exhibit a negligible photocatalytic  $\text{H}_2$  generation ( $0.06 \mu\text{L h}^{-1} \text{cm}^{-2}$  and  $0.14 \mu\text{L h}^{-1} \text{cm}^{-2}$ , respectively). The slight improvement of the  $r_{\text{H}_2}$  may be ascribed to electron-hole separation at the  $\text{TiO}_2/\text{WO}_3$  interface, which can make electrons more available for the  $\text{H}_2$  evolution (spatially separated charges). As expected,  $\text{Pt-TiO}_2$  photocatalyst ( $1\text{Pt-TiO}_2$ ) shows an improved  $\text{H}_2$  evolution compared to pristine  $\text{TiO}_2$ , i.e. leading to a  $r_{\text{H}_2}$  of  $3.4 \mu\text{L h}^{-1} \text{cm}^{-2}$ . This effect is due to the formation of  $\text{Pt/TiO}_2$  Schottky junctions at the  $\text{TiO}_2$  nanotubes top.

Nevertheless, a substantial further enhancement of the photocatalytic performance is obtained modifying  $\text{TiO}_2$  with both  $\text{WO}_3$  and Pt ( $1\text{Pt-xWO}_3\text{-TiO}_2$ ), that is, by constructing a stacked  $\text{Pt-WO}_3\text{-TiO}_2$  architecture at the NT top. In particular, photocatalysts with 1, 3 and 5 nm of  $\text{WO}_3$  lead to the highest  $\text{H}_2$  generation rates, that is, of 4.4, 5.0 and  $5.2 \mu\text{L h}^{-1} \text{cm}^{-2}$ , respectively. Note that these  $r_{\text{H}_2}$  can be up to a factor 1.5 higher than that of  $1\text{Pt-TiO}_2$ . Long-run photocatalytic tests (carried out by continuous irradiation for 30 h – Fig. 4c) reveal that the  $r_{\text{H}_2}$  remains constant and thus, deterioration phenomena such as photocorrosion of the photocatalyst or fall-off of the cocatalytic Pt NPs can be ruled out.

Taking into account the band edge alignment and energetic situation of the elements of the  $\text{Pt-WO}_3\text{-TiO}_2$  triad, one can interpret these photocatalytic results assuming that the defined  $\text{Pt-WO}_3\text{-TiO}_2$  architecture constructed at the top of the NT walls enables efficient electron transfer from the  $\text{TiO}_2$  NTs (light absorber and charge carrier generator) to the  $\text{WO}_3$  top layer, and then onward to the Pt cocatalytic NPs. This “electron transfer cascade” is therefore the main cause for the observed synergistic  $r_{\text{H}_2}$  enhancement.

A side effect of the site-selective decoration of the NT top only (W films  $< 10$  nm) is that the bottom of the  $\text{TiO}_2$  nanocavities is left uncovered, i.e. free  $\text{TiO}_2$  surface. This situation, along with the intrinsic upward band bending in the nanotube walls [50] and the typically short diffusion length of holes in  $\text{TiO}_2$ , leads to direct hole-transfer to the reactants (ethanol), which reduced the electron-hole recombination in the NTs.

In order to corroborate the results of photocatalytic  $\text{H}_2$  evolution and their interpretation, photo-degradation tests of Acid Orange 7 (AO7) under 365 nm UV light irradiation were carried out with the reference materials  $1\text{Pt-TiO}_2$  and  $3\text{WO}_3\text{-TiO}_2$ , and different three-layered structures, i.e.,  $1\text{Pt-}3\text{WO}_3\text{-TiO}_2$  and  $1\text{Pt-}30\text{WO}_3\text{-TiO}_2$ . The results are reported in Fig. 4d and e. Noteworthy, also in this case, for single-cocatalyst structures, the deposition of a noble metal ( $1\text{Pt-TiO}_2$ ) leads to a significantly higher AO7 photocatalytic degradation rate compared to the modification with  $\text{WO}_3$  ( $\text{WO}_3\text{-TiO}_2$ ). More importantly, the  $\text{Pt-WO}_3\text{-TiO}_2$  triad with optimized amount of W ( $\sim 1\text{--}5$  nm) leads to a higher photocatalytic performance (AO7 degradation) compared to  $1\text{Pt-TiO}_2$ . However, a too large amount of W ( $\sim 30$  nm) leads to a lower AO7 degradation rate. In other words, these data are fully in line with the  $\text{H}_2$  evolution results.

In order to understand the role of the  $\text{WO}_3$  top layer and of the thickness on the photocatalytic performance, the light absorption properties of the different structures along with their photo-electrochemical behavior were investigated by measuring UV–vis diffuse reflectance (DR UV–vis) and photocurrent spectra (see Figs. 5 and S5, respectively). Interestingly, only minor differences in terms of light absorbance between the various morphologies were observed at 365 nm (Fig. 5). Besides, the photocurrent trend observed in the photo-electrochemical measurements is:  $\text{TiO}_2 > 3\text{WO}_3\text{-TiO}_2 > 1\text{Pt-}3\text{WO}_3\text{-TiO}_2 > 1\text{Pt-TiO}_2$  (Fig. S5). In other words, in a photo-electrochemical configuration, photo-anodes consisting of pristine nanotube arrays outperform any other cocatalyst-decorated structures (additional discussion is given in the supplementary information). Also, a virtually

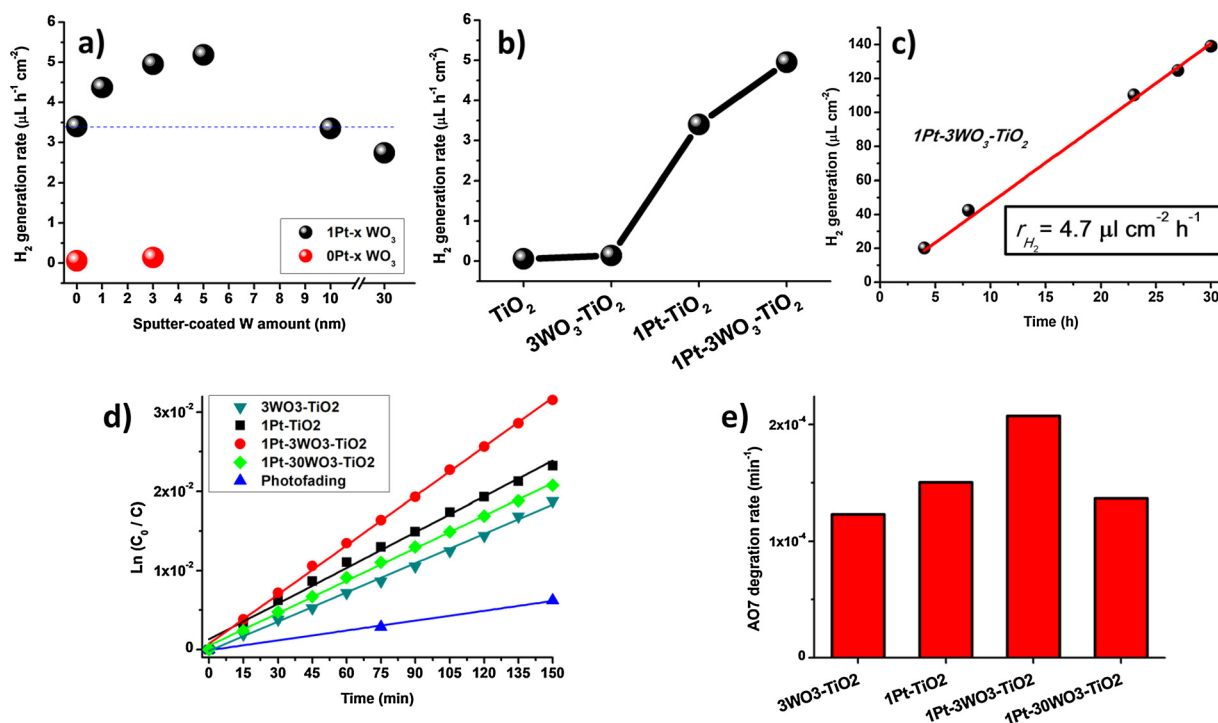


Fig. 4. (a) Photocatalytic H<sub>2</sub> evolution results of different TiO<sub>2</sub> nanotube structures as a function of sputtered W amount; (b) summary of the  $r_{H_2}$  improvement achieved with an optimized Pt and WO<sub>3</sub> decoration on the top of the TiO<sub>2</sub> NT arrays. (c) Evaluation of the photocatalytic H<sub>2</sub> evolution performance of 1Pt-3WO<sub>3</sub>-TiO<sub>2</sub> over an irradiation time of 30 h. (d) First-order kinetic fitting for the photocatalytic degradation (oxidation) of AO7 (Acid Orange 7) using different TiO<sub>2</sub> nanotube structures. (e) AO7 degradation rates for the different samples.

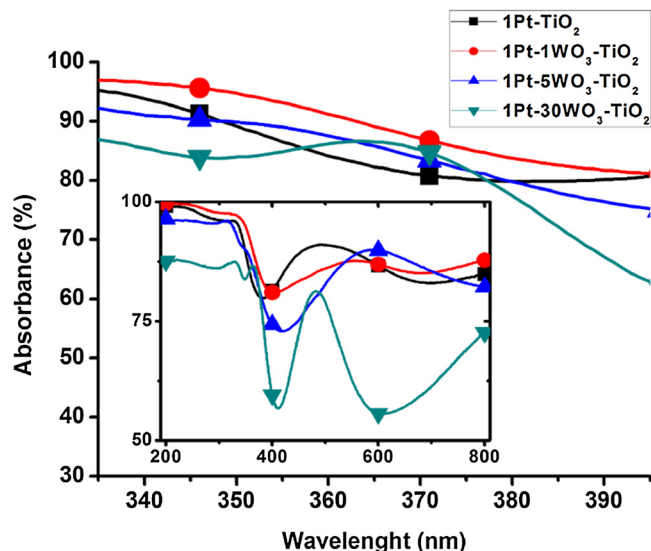


Fig. 5. Detail of the DR UV-vis spectra of different TiO<sub>2</sub> structures in the region around 365 nm (i.e. wavelength used in this work for the photocatalytic experiments). Inset: DR UV-vis spectra measured in the 200–800 nm wavelength range.

identical bandgap of 3.0 eV can be estimated for the various structures, which is in line with that of anatase TiO<sub>2</sub>.

Considering these results, it is clear that the light harvesting ability of the different structures (i.e. different W loadings) does not have a dominant effect on the photocatalytic performance – here, it is reasonable to assume that WO<sub>3</sub> is not the photoactive material in this photocatalytic architecture, but acts as a buffer (transfer) layer for TiO<sub>2</sub> electrons, and the contribution of charges generated directly in WO<sub>3</sub> to H<sub>2</sub> evolution may be negligible.

Thus, one can assume that the Pt-WO<sub>3</sub>-TiO<sub>2</sub> structure is properly constructed only when the WO<sub>3</sub> top layer is sufficiently thin: in this case it can favor charge carrier separation by electron transfer towards the top of the tube, through the WO<sub>3</sub> buffer layer, and then onward to the Pt NPs for H<sub>2</sub> evolution. The energetic situation was confirmed by XPS valence band measurements (Fig. S6) that show similar valence band maxima for both TiO<sub>2</sub> (nanotubes) and WO<sub>3</sub> (buffer layer) – that is, the WO<sub>3</sub> CB minimum lies in this photocatalytic architecture above the redox potential of water, as illustrated in Fig. 6.

In this construction, crucial is also the uncoated bottom of the TiO<sub>2</sub> cavities that allows for direct hole-transfer to the reaction phase (hole-scavenging). This explains also the low H<sub>2</sub> yield of the sample 1Pt-30WO<sub>3</sub>-TiO<sub>2</sub>, that is, a too thick WO<sub>3</sub> buffer layer not only blocks TiO<sub>2</sub> hole-transfer to the environment at the tube bottom, but also can make less efficient the electron transport across the WO<sub>3</sub> layer owing to an increased charge transfer resistance. These findings are in line with the

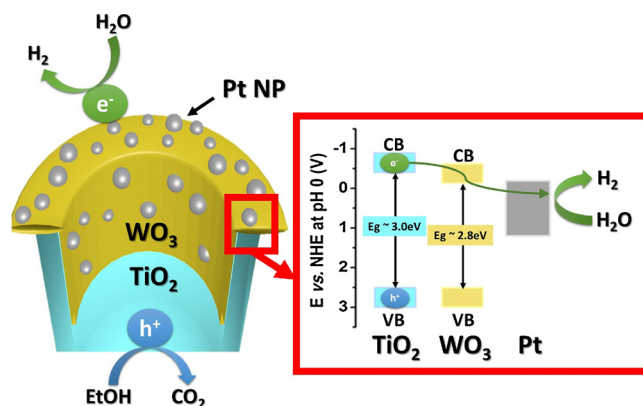


Fig. 6. Scheme of the structure of the three-layered photocatalyst illustrating the band alignment (TiO<sub>2</sub>-WO<sub>3</sub> [51] energetic situation) that allows for the proposed mechanism of electron transfer cascade.



proposed electron transfer cascade mechanism, and well support EIS results obtained for similar stacked-architectures [13] for which charge accumulation can be observed in WO<sub>3</sub>-TiO<sub>2</sub> structures under UV light illumination (TiO<sub>2</sub> CB electrons are transferred to WO<sub>3</sub>), while the accumulated charge is depleted when Pt nanoparticles are decorated atop the WO<sub>3</sub> buffer layer (in the Pt-WO<sub>3</sub>-TiO<sub>2</sub> architecture electrons are extracted by Pt and transferred to the environment for H<sub>2</sub> evolution).

#### 4. Conclusions

We introduced the fabrication of an efficient photocatalytic platform based on an electron transfer cascade mechanism designed by site-selective decoration of the top of highly-ordered TiO<sub>2</sub> nanotubes with a well-defined Pt-WO<sub>3</sub> cocatalyst stack. We show that a morphological control with nanoscale precision of the cocatalyst-catalyst structure not only allows for a systematic assessment of the charge carrier dynamics and photocatalytic mechanism, but also is key to design functional composite architectures that can achieve strongly enhanced photocatalytic H<sub>2</sub> evolution efficiencies.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.05.061>.

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